On the Reactions of Both the Ions and the Nonionized Forms of Electrolytes: On the Reactions of Methyl Iodide with Sodium, Potassium and Lithium Ethylates at 0° and 25°.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

BESSIE MARION BROWN

BALTIMORE

June, 1913

MADISON, WISCONSIN

STATE JOURNAL PRINTING CO.

1915

Diss.
Baltimore
1913

75N53

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ACKNOWLEDGMENT

The author takes this opportunity to express her gratitude to Professor Remsen, Professor Morse, Professor Jones, Professor Whitehead, Associate Professor Acree, Associate Professor Lovelace and Dr. Frazer for valuable instruction.

Special thanks are due to Associate Professor Acree, at whose suggestion and under whose guidance this work was carried out.

On the Reactions of Both the Ions and the Nonionized Forms of Electrolytes.

THEORETICAL

An entirely new theory concerning chemical reaction was brought out by Acree and Brunel[1] in 1905–06, and Acree and Johnson[2] in 1907, when they showed by experimental evidence that, in some catalytic reactions, the acceleration may take place not only through the action of the ions, but also *to a large extent* through the nonionized portion of the salt.

The work of Shadinger,[3] and later Nirdlinger and Rogers,* and Chandler,† showed that in absolute alcohol both the 1–phenyl–3–thiourazole anions and the nonionized sodium 1–phenyl–3–thiourazole react with alkyl halides.

In working with the phenolates, Robertson [4] found that both the phenolate ion and the nonionized sodium phenolate react with the alkyl halides, and Marshall, Harrison,[5] and Myers observed that both the ions and molecules of sodium potassium and lithium ethylates are concerned in the catalytic effect of these compounds on the reversible addition of alcohol to acetonitrile, benzonitrile, para brombenzonitrile and others.

Other reactions studied, and which uphold this theory, are those of methyl iodide, ethyl iodide, and ethyl bromide with sodium, lithium, and potassium ethylates at 25°.

Any results which shed light upon the mechanism of organic reactions are of such extreme importance, that it was considered advisable to extend this study to other reactions, and to study some of the same reactions at different temperatures.

With this idea in view, the author took up the study of the reactions of sodium, lithium and potassium ethylates with methyl iodide at 0°, and also the effect of added sodium iodide on the reaction between sodium ethylate and methyl iodide at 25°.

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[1] Am. Chem. J., **43**, 505.
[2] Ibid., **38**, 259, 260.
[3] Ibid., **39**, 275.
* Am. Chem. Jour. **49**, 116.
† Diss., J. H. U., 1912.
[4] Diss., J. H. U., 1910.
[5] Diss., J. H. U., 1912.

If both the ethylate ion and the nonionized ethylate salt react with the molecular alkyl halide, we have two reactions proceeding simultaneously, one proportional to the ionized part of the ethylate, a, and the other proportional to the nonionized part, $1 - a$. It follows that

$$(1)\quad dx/dt = K_i a(C_{\text{ethylate}} - x)\ (C_{\text{alkyl halide}} - x) + K_m(1 - a)\ (C_{\text{ethylate}} - x)\ (C_{\text{alkyl halide}} - x)$$

in which K_i is the velocity constant for the ionic reaction, and K_m is the constant for the molecular reaction in a normal solution, and x is the change in the concentration in the time t. If A represents C_{ethylate}, and B is substituted for $C_{\text{alkyl halide}}$ we obtain by integration the equation

$$(2)\quad K_N = K_i a + K_m(1 - a) = \frac{1}{At}\ \frac{x}{(A - x)} \quad \text{if } C_{\text{ethylate}}$$

is equal to $C_{\text{alkyl halide}}$, or

$$(3)\quad K_N = K_i a + K_m(1 - a) = \frac{(B - A)t}{1}\ \ln\ \frac{A(B - x)}{B(A - x)}$$

if C_{ethylate} is not equal to $C_{\text{alkyl halide}}$.

Substituting the data obtained for t, x, A, and B, we obtain a set of constants for K_N for each concentration of ethylate used. K_N represents the molecular velocity constant, or the velocity which that reaction would have if the concentration were normal, but the ionization corresponded to the concentration $1/V$, when V is the number of liters containing one gram molecule. For a complete mathematical and theoretical discussion of these equations, see Johnson and Acree,[6] and dissertations of Robertson, and Harrison.

To determine K_i and K_m for the separate ionic and molecular reactions, it is only necessary to substitute the proper values in the following simultaneous equations and solve for K_i and K_m.

$$K_N = K_i a + K_m(1 - a)$$
$$K_N' = K_i a' + K_m(1 - a'), \text{ etc.}$$

Values for K_i and K_m are thereby obtained for every pair of

[6] Am. Chem. J., **37**, 410; **38**, 258; **48**, 352.

concentrations, and the average of these is taken as the accepted value.

Robertson discussed the possibility and probability of other reactions taking place simultaneously with those given above. We must consider, for example, the catalytic effect of the salt formed, or even of the ethylate itself, which we could designate as a "salt effect," and perhaps a side reaction, as well, in which olefines may be formed.

Since we obtain, however, from the equations used two constant values for K_i and K_m, we can state that we have either two reactions, or two or more sets of reactions, taking place, one being a function of the concentration of the ions, and the other of the nonionized portion.

If K_i represents the velocity constant of the reaction between the ethylate ion $C_2H_5\bar{O}$ and methyl iodide, we would expect to find experimentally that the value for K_i is the same whether the methyl iodide is allowed to react with sodium, lithium, or potassium ethylates, although the values for K_m would not necessarily be the same, and might be entirely different, because of the fact that the nonionized molecules of these three ethylates are different substances.

Probably the best evidence in favor of this theory is the fact that identical values are obtained for the ethylate ion irrespective of the ionization of the ethylate, the character of the metal, and of the value for K_m. For methyl iodide and sodium ethylate at 25°, Robertson obtained the values $K_i = 0.127$, and $K_m = 0.0594$. The author repeated this work at the very beginning of this investigation, and obtained the values $K_i = 0.128$ and $K_m = 0.0586$. For potassium ethylate and methyl iodide at 25°, Harrison obtained the values $K_i = 0.127$ and $K_m = 0.066$. Similar agreement is found for the phenolate ion when potassium, lithium, and sodium phenolates react with methyl iodide and ethyl iodide.

At 0° the velocity of the reaction is very much less, but we should expect to find that the values for K_i at this temperature is the same whether sodium, lithium, or potassium ethyl-

ates are used. Considering the greater difficulty in carrying out these reactions at 0° and the possibility of greater errors, the agreement between the values of K_i for the different ethylates is quite satisfactory. Since viscosity may play an important part in the reaction velocities at 0°, especially in the more concentrated solutions, it will be extremely interesting, as well as important, to obtain all the necessary data, so that corrections can be made for the viscosity.

In Tables I–XV of the lithium series the starred values for K_N are obtained by discarding those constants which correspond to reactions which were allowed to run over night. In these cases the reactions were more nearly complete, the result being that the constants had dropped several per cent. A slight drop was always noticed, but this was usually negligible, or very small, in the dilute solutions. For a fuller discussion of the probable causes for this drop in the constants during any specific reaction, see the dissertation of Robertson.

To make the constants from the different concentrations of ethylate comparable, the reactions were allowed to run to about the same percentage completion, which was usually 50 to 60 per cent, and an average value for the reaction velocity was obtained by taking the mean of the constants for the different time periods. It will be seen from the results that it makes very little difference in the calculated values for K_m when these starred values are used in place of the other values.

In the case of lithium ethylate the reaction was so much slower than in the other cases, that it was difficult to obtain the desired time periods, since it was, of course, impossible to titrate by artificial light. For this reason, in some of the more dilute solutions the reactions were 70 to 80 per cent completed. But since the constants in these solutions did not decrease appreciably, there is practically no error introduced by using these values for the longer time periods.

It can be seen from the tables that there is very little difference between the values of K_N for the different concentrations of potassium ethylate, and that in some of the more dilute so-

lutions, the values vary to such an extent that they nearly overlap for the different concentrations. The only remedy for this is to diminish the error as much as possible by taking the average of a large number of determinations. It was impossible to use solutions more concentrated than N/4 because the potassium iodide formed precipitated out almost immediately, and the ionization of the remaining potassium ethylate consequently changed. It was therefore thought advisable to find values of K_N for 3N/16 and 3N/32 potassium ethylate so as to give a few more calculated values for K_i and K_m and reduce the error.

By substituting in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$, these values found for K_i and K_m and the values for α and $1 - \alpha$ corresponding to the different concentrations of the various ethylates, we obtain the theoretical values for K_N given on page 28 under the heading "K_N calculated." These are compared with the corresponding values of "K_N found," and the experimental errors are thus obtained.

It can be seen from the data given that the work at 0° is not quite as satisfactory as that at 25°.

Salt Effect

Although many theories have been advanced concerning the so-called "salt effect" of neutral salts on certain organic reactions, through lack of sufficient data no very satisfactory explanation has yet been reached.

From the results obtained during the last ten years in this laboratory, however, we can at least point out many errors in the earlier work, and present our own conclusions which seem to be capable of wider application.

The view adopted by Euler[7] in 1900 was in accordance with the belief of Arrhenius[8] that the salt cation produces this salt effect by causing a change in the ionization of the water. This was the explanation given by Stieglitz to explain the phenom-

[7] Z. Physik. Chem., **32**, 348.
[8] Ibid., **1**, 110; **4**, 226; **31**, 197.

enon of salt catalysis which he found in studying the hydrolysis of imidoester salts.[9]

In a full discussion of the subject, Acree[10] has shown that the explanation offered by Euler and Stieglitz is contrary to facts, one of the strongest points against this theory being the experimental data showing that this view calls for a change in the ionization of water many times greater than could possibly be brought about in this way. According to their theory, the same salt in the same concentration should sometimes cause an increase, and sometimes a decrease in the ionization constant of water.

It is believed by Acree, and this idea is shared by others (see Lapworth[11]), that salt catalysis is a very complex phenomenon, and involves a large number of factors, both chemical and physical, one of the least important being perhaps the change in ionization of the solvent. In the same article mentioned above,[12] some of these different factors which are probably concerned in any salt effect are fully discussed.

In this laboratory, different investigators have studied the effect of certain added salts on the reactions of the alkyl halides with phenolates, ethylates, and urazole salts. They found that the greater part of the effect was perfectly normal in that it corresponded to the change in ionization of the reacting substances, produced by the added salt. In some cases, however, a small deviation from the calculated amount was observed which was designated as an "abnormal salt effect," and which might be either "positive" or "negative."

Harrison,[13] in studying the formation of nitriles from imidoesters by using sodium ethylates as a catalyzer, found that the addition of even several moles of sodium iodide lowered the percentage of ionization of the sodium ethylate, and hence the reaction velocity, as calculated, which fact shows that the "salt effect" here was "normal." Since in this case K_i and

[9] Am. Chem. J., 39, 29, 166, 402, 437, 586, 719. J. Am. Chem. Soc., 32, 221.
[10] Am. Chem. J., 41, 475.
[11] Chem. News, 97, 310.
[12] Am. Chem. J., 41, 478–483.
[13] Dissertation, J. H. U., 1912.

K_m are so nearly equal, even the "normal salt effect" was extremely small.

Robertson[14] found in the reaction of sodium phenolate with certain alkyl halides, that added sodium iodide produced a "positive abnormal salt effect," in other words, the velocity constant was slightly larger than the calculated value.

On the other hand, Chandler[15] found that sodium iodide produces practically the calculated effect on the reaction between 1–phenyl–3–thiourazole and ethyl iodide.

The results obtained by adding different amounts of sodium iodide to the reaction between methyl iodide and sodium ethylate and 25° are shown in Tables LXXXIV–CXIII and in tabulated form on pages 48–55. In the first column will be found the volume containing a gram equivalent of the sodium ethylate. In the second column is the reciprocal of the concentration of the sodium iodide added, and the third column gives the reciprocal of that concentration of sodium ethylate or sodium iodide having the ionization calculated for either of these electrolytes in the mixture by the use of the isohydric principle.

To give a concrete example of the method used in obtaining the calculated values of K_N, let us consider the case of a solution which is N/32 with reference to both sodium ethylate and sodium iodide. According to the isohydric principle, each electrolyte occupies that portion of the solution which is in proportion to the number of ions it furnishes. In this case, then, since the sodium ethylate and sodium iodide are ionized to approximately the same extent, we can say that each of these ionized constituents occupies half of the solution, and the sodium ethylate consequently would have the ionization of a N/16 solution. Then in the equation $K_N = K_i\alpha + K_m(1 - \alpha)$ we would substitute the values of α and $1 - \alpha$ for a N/16 ethylate solution. If the effect of the sodium iodide is perfectly normal, this is the value of K_N which we should obtain experimentally.

[14] Dissertation, J. H. U., 1910.
[15] Dissertation, J. H. U., 1912.

It can be seen from the values for K_N found that in every case, the constant obtained is lower than that calculated, the difference being the "auto" or "abnormal" salt effect, which is expressed in the last column as a percentage of the theoretical constant. Since the constant is lower than the theory, the catalytic effect of the salt is negative and must decrease the velocity of the reaction.

With any one concentration of ethylate, as for instance with the N/32 solution, the "auto" effect increases with the concentration of the added iodide, but not in a direct proportion. That is, although the addition of 3/32 mole of sodium iodide produces approximately three times the effect of 1/32 mole of added salt, and 7/32 mole about seven times as great an effect as the 1/32 mole, this relationship does not continue to hold, for 15/32 mole produces only eight times, and 31/32 mole only twelve times as great an effect as does the 1/32 mole of sodium iodide. In a similar way, with the N/16 sodium ethylate, while 3/16 mole of added salt produces nearly three times the effect of 1/16 mole, 7/16 mole gives only three and one-half times, and 15/16 mole only six times as great an effect.

These figures naturally suggest that the "auto" effect is a function of the ionized portion of the added salt, since the effect decreases with increased concentration in the same manner as would be expected from the suppression of the ionization. It will be shown in equations developed below that the greater portion of the "abnormal" effect of the salt does appear to be a function of the iodide ions.

It must be constantly borne in mind in applying this data to such generalizations, that the "abnormal" salt effect is only a very small part of the whole effect of the salt on the reaction velocity, and since the numerical value of this "auto" effect is obtained by subtracting the K_N found from K_N calculated, an error of one per cent in the velocity constant would constitute an error of fifty per cent in the "abnormal" salt effect obtained by adding 1/32 mole of sodium iodide to

the N/32 sodium ethylate. Consequently from these figures only an approximation can be made concerning the actual effect of the salt, but we can at least obtain some idea of the direction and magnitude of this effect.

By taking the sum of all the percentage lowerings found in the case of N/32 ethylate and dividing this sum by 57, since 57/32 moles of sodium iodide were added in all, we obtain as a result 1.15, which can be considered the average effect of 1/32 mole of sodium iodide in a N/32 ethylate solution. In the same way we obtain 0.86 as the average effect of 1/32 mole of sodium iodide in the N/16 ethylate, 0.74 for the N/8 ethylate, and 0.65 for the N/4 solutions. It would appear that the salt effect is not merely a function of the added iodide but of the ethylate concentration as well. These facts seem to contradict the Spohr[16] hypothesis. His work seemed to show that a definite concentration of sodium chloride added to different concentrations of hydrochloric acid produced a specific effect on the reaction velocity of the inversion of cane sugar, irrespective of the concentration of the acid, and therefore of the actual velocity of the reaction.

If the ethylate ion, $C_2H_5\bar{O}$, and the iodine ion, $\bar{I}$, each has an independent catalytic effect on the two reactions taking place which we represented by K_i and K_m, we could then express this condition by the following equation,

$$K_N = [K_i a + K_m(1 - a)]\ [1 + K_s C_s a' + K_e C_e a]$$

in which K_N represents the actual velocity constant obtained when sodium iodide is added, and K_s and K_e are the constants referring to the catalytic effect of the iodide and ethylate ions, respectively. C_s is the concentration of the added salt, a' its ionization, C_e the concentration of the ethylate, and a its ionization. By substituting the found values for K_N and the known values for K_i, K_m, a, $1 - a$, and a', we obtain a series of simultaneous equations which can be solved for K_s and K_e. The values for K_s and K_e obtained were constant in most

[16] J. prakt. Chem., **32**, 32; **33**, 265.

cases. It must be understood that the error in certain cases might be such as to give values for K_s and K_e which did not seem to fit into this scheme. If we take $K_s = -70$ and $K_e = -40$ as averages for the values thus obtained, we can then substitute them in the above equation and calculate our values for K_N, which we should obtain experimentally if the equation holds. Table CXVI on page 58 shows the calculated and found values with the percentage error.

EXPERIMENTAL

Preparation of Materials

The method used in preparing the solutions and carrying out the reactions at 25° is described in detail by Robertson.[17]

The methyl iodide used was of special purity obtained from Hoffmann and Kropff. To insure a large yield of a constant boiling material, two kilograms of the alkyl halide were shaken with dilute sodium carbonate solution to remove any traces of hydriodic acid, washed twice with water, and then shaken for a few minutes with anhydrous sodium sulphate, and filtered through glass wool. A considerable quantity of phosphorus pentoxide was added and allowed to remain over night, after which the methyl iodide was distilled. This treatment with the phosphorus pentoxide was repeated, and the product thus obtained was fractionated. Special care was taken to have the condenser and all apparatus perfectly dry, and with these precautions, a product was obtained, the total quantity of which boiled within a few hundredths of a degree. A table is given below showing the boilings points of the different fractions, the barometric pressure and the boiling points at 760 millimeters after all the necessary corrections are made.

[17] L. c.

Observed B. pt.	Barometer	Corrected B. pt.
42.80 — 42.83°	769.4 mm	42.31 — 42.33°
42.82 — 42.82	769.3	42.33 — 42.35
42.82 — 42.81	769.3	42.34 — 42.33
42.81 — 42.81	769.2	42.33 — 42.33
42.93 — 42.91	771.2	42.35 — 42.35
42.91 — 42.86	770.6	42.35 — 42.35
42.86 — 42.82	769.5	42.35 — 42.34
42.82 — 42.80	768.9	42.34 — 42.34
42.80 — 42.78	768.2	42.34 — 42.36
42.78 — 42.79	767.7	42.36 — 42.37

The rise in boiling point observed in the last fraction was probably due to superheating. No correction was necessary for the exposed stem because the distilling flask with a long neck made especially for the purpose was used, which made it possible to surround the total column of mercury with the vapor of the alkyl halide. In correcting for the atmospheric pressure the value used was 0.03° per millimeter. The total amount of methyl iodide recovered in these ten fractions was 1,772 grams out of the 2,000 grams used. This is a very satisfactory yield for such a volatile substance. In order to decrease the loss due to the volatility of the methyl iodide, ice-water was continually run through the condenser by means of a fine lead coil of several turns surrounded by ice, and the receiving bottles cooled by ice-water and fairly tightly stoppered with cotton. It was not usual for the boiling point to become constant at the very beginning of the distillation, as did the above samples.

From another sample of methyl iodide from the same source which had been treated in a similar manner but without the special precautions taken for excluding moisture from all apparatus and for preventing the loss of methyl iodide, only about 1,250 grams were obtained. This has a boiling point of 42.33 — 42.37°, most of which, however, came over at 42.34 — 42.36°, which is identically the same boiling point obtained in the sample mentioned above. The lower yield was

partly due to the fact that the methyl iodide was digested twice for nearly a whole day on a water bath in the presence of phosphorus pentoxide, and it was impossible to prevent entirely the escape of the vapor from the connections and also from the top of the condenser. It was afterwards found that this heating was entirely superfluous, as a sample which simply stood over night with phosphorus pentoxide gave a very satisfactory boiling point.

Another sample from Hoffmann and Kropff, treated in a similar way, but without the special precautions, and distilled with the mercury column exposed, gave the corrected boiling point of 42.30 — 41.32°. There is no doubt in the author's mind that this discrepancy is principally the result of errors in correcting the boiling point and that the sample was practically as good as those mentioned above.

One sample of good methyl iodide which had stood during the summer was distilled once from phosphorus pentoxide and then fractionated; it gave a large middle portion which boiled at 42.34 — 42.36°. Another sample of methyl iodide which was made in the laboratory by the method described by Robertson, gave a fraction boiling at 42.35 — 42.39°.

It would seem from the boiling points obtained that the methyl iodide used in the reactions was of especial purity. Nevertheless, it was not only a wise precaution but a point of great interest to determine the composition of such samples by analysis.

Analysis of Methyl Iodide

At first an attempt was made to use small glass bulbs which were filled with the sample, sealed, weighed, and then broken by means of a glass rod in an excess of a 2 N solution of sodium ethylate contained in a small flask, the latter being afterward corked and warmed at about 60°. After the reaction was complete the solution was acidified and the iodine was precipitated as silver iodide.

AgI Obtained	AgI Calculated	Per Cent Error
1.0236 gms.	1.0264 gms.	—0.3
2.1841	2.1938	—0.5

Either loss of alkyl halide occurred during the heating, or moisture was absorbed by the methyl iodide while the bulb was being filled.

Much more satisfactory results were obtained by using small weighing tubes with ground glass stoppers which were especially made for the purpose and held about two cubic centimeters. The alkyl halide could thus be weighed accurately and without loss. The weighing tube containing the alkyl halide was then placed in a regular Carius tube containing an excess of sodium ethylate, sealed, and heated a sufficient length of time in a water bath. It was necessary, of course, to mix the contents thoroughly before heating. The stopper in the little weighing tube was easily removed by warming the tube slightly and then shaking it gently. When the reaction was complete the contents of the tube were washed into a beaker, and then filtered into a calibrated flask, diluted to the mark and weighed. Each portion taken out for analysis was then weighed, since this procedure was much more accurate than the volume method.

Sample I

AgI Obtained Air Wt.	AgI Calculated Vacuum Wt.	Per Cent Error
2.0346 gms.	2.0327 gms.	+0.12
2.0336	2.0339	+0.01
1.9956	1.9953	+0.04

Sample II

A

AgI Obtained	AgI Calculated	Per Cent Error
1.5890 gms.	1.5889 gms.	+0.02
1.5886	1.5889	0.00
1.5894	1.5898	0.00

	B	
1.7232 gms.	1.7243 gms.	—0.03
1.7264	1.7280	—0.08
1.7271	1.7273	+0.01
	C	
1.5493 gms.	1.5500 gms.	—0.03
1.5489	1.5495	—0.02
1.5488	1.5499	—0.05

In the above analyses Sample I and Sample II are taken from different samples of methyl iodide.

It is seen that we can easily make alkyl halides with a high degree of purity and that this method of analysis is very accurate. The Per Cent Error is corrected to vacuum weights.

Preparation of Solutions for Salt Catalysis

The alcohol used contained from 0.02–0.04 per cent of water. The preparation of this alcohol has been previously described by Robertson, as was also the regulation of the bath at 25°, and the mode of procedure used in determining the velocity constants at this temperature.

The solutions for the experiments on the salt effect were usually prepared by making a sodium ethylate solution having a strength slightly greater than that desired. The calculated number of cubic centimeters of the solution, say 90–95 c. c., were put into a 100 c. c. flask which already contained the amount of sodium iodide required, diluted to the mark, and then 10 c. c. of this was titrated to obtain the value of *A*. A very small excess of the ethylate solution was usually added to be sure that the resulting solution was not too dilute. If too concentrated, the calculated amount of alcohol was added; if this was more than a few tenths of one cubic centimeter, more sodium iodide was added as well. The amount of salt added in these cases was too small to introduce any appreciable error in the volume.

Calibration of the Machine

Since methyl iodide is so very volatile it would be impossible to transfer the solution to the reaction flasks by the use

of an ordinary pipette, without losing a large amount of the alkyl halide. A special apparatus called the "machine" was devised to transfer these solutions with the least possible loss. This machine was described in detail by Robertson.

The machine pipette was first marked to deliver 10 c. c. of absolute alcohol at 20° and the volume obtained was 10.004 c. c., the error being less than 0.1 per cent. Since this pipette was to be used for alkyl halide solutions, the author wished to determine whether the same volume of methyl iodide solution would be obtained. The specific gravity of the methyl iodide solution was determined and successive portions of 10 c. c. each were then run out into the same small flasks used for reactions, and weighed. These flasks were closed by corks but it had been shown previously that the reaction mixture did not escape, and in this case it was found that these flasks containing the volatile methyl iodide solution could be weighed without loss. The volumes of N/2 and N/4 alkyl halide solutions obtained at 25° were 10.00, 9.997, 9.982, 9.992, 9.996, and 9.990 c. c. The average of these is 9.993 c. c. and was considered as sufficiently near to the desired volume. Although this difference is probably within the experimental error, yet it is quite possible that the alkyl halide solution is slightly more viscous and does not drain as readily.

When using this same machine at 0° the pipette was recalibrated with a methyl iodide solution at this temperature. The volumes obtained were 9.979, 9.981, 9.971, 9.975, and 9.974 c. c., the average being 9.976 c. c. In all of the work at 0° the solution was run out to a point on the pipette which would deliver exactly 10 c c. at this temperature.

Determination of Loss of Alkyl Halide

An investigation was also carried out to determine whether it was necessary to keep the tip of the delivery tube below the surface of the liquid in the reaction flask while introducing the alkyl halide solution. No vacuum corrections were made.

AgI Obtained	AgI Calculated	Strength of Solution	Percentage Error	Position of Tip
2.3483	2.3550	(100.3%)	—0.28	Below surface of liquid.
2.3374	2.3550	(100.3%)	—0.75	Just below neck of flask.
2.3330	2.3550	(100.3%)	—0.90	Near top of neck.
2.3455	2.3550	(100.3%)	—0.40	Just below neck.
2.3330	2.3550	(100.3%)	—0.90	Half way down neck.

These figures show that it is certainly necessary to keep the tip well under the surface of the liquid.

A large number of determinations were also carried out to see whether the three-tenths per cent excess of methyl iodide ordinarily added was sufficient to make up for any loss of the alkyl halide during the preparation and transfer of the solution. While keeping the conditions the same as those used for studying the reactions, 10 c. c. of the solution was run into a small reaction flask containing a 50 per cent alcoholic solution of silver nitrate. The results obtained are given in the tables below. The calculated values given for the silver iodide include the excess added which is given in the parentheses under "Strength of solution."

AgI Obtained	AgI Calculated	Strength of Solution	Per Cent Error
2.3535 gms.	2.3550 gms.	(100.1%)	—0.06
2.3500	2.3550	(100.1%)	—0.21
2.3424	2.3550	(100.1%)	—0.11
2.3570	2.3620	(100.6%)	—0.21
2.3533	2.3597	(100.5%)	—0.27
1.1727	1.1775	(100.3%)	—0.40
1.1712	1.1775	(100.3%)	—0.53
		Average =	—0.26

At 0°

AgI Obtained	AgI Calculated	Strength of Solution	Per Cent Error
*1.1743 gms.	1.1799 gms.	(100.5%)	—0.47
*1.1729	1.1799	(100.5%)	—0.60
*1.1730	1.1799	(100.5%)	—0.60
2.3584	2.3598	(100.5%)	—0.06
4.7279	4.7288	(100.7%)	—0.02
2.3576	2.3621	(100.6%)	—0.20
2.3583	2.3621	(100.6%)	—0.16
2.3542	2.3598	(100.5%)	—0.22
4.7057	4.7101	(100.3%)	—0.09
2.3495	2.3598	(100.5%)	—0.43
			——
* Same solution.		Average =	—0.27

The average of the above analyses shows that the 0.3 per cent excess of methyl iodide seems to be sufficient, although there is considerable variation in the results. However, in a number of reactions 0.5 per cent excess was added.

Reaction Velocities at 0°

For the study of the velocity of the reaction between methyl iodide, sodium, lithium, and potassium ethylates at 0° an ice bath was used which gave very satisfactory results. This consisted of a copper bath ten inches deep and fourteen inches in diameter which was tinned on the inside, and placed in a wooden box containing lamb's wool. The bottom was protected with a thick felt pad about one inch thick, and the top, by a tightly fitting metal cover over which were placed several pads of felt and wool. The metal cover was made in two pieces, one of which was removed when it was necessary to take out the flask, start the reaction, etc. Special attention is called to the stirring device. The motor is supported by an iron framework which is bolted firmly to the wall to prevent vibration. Motion is imparted to the propeller shaft by a friction pulley, by means of which the speed can be easily controlled.

Tests with a Beckmann thermometer showed that all parts of the bath remained within a few thousandths of a degree of zero. The ethylate solutions were made up at 0°, and transferred at this temperature into the reaction flasks by surrounding the pipette with a jacket containing cracked ice and water. In beginning this work the jacket of the machine pipette was filled only once or twice with ice water during the seven or eight minutes required for running out all of the alkyl halide solution. The reaction flask containing the ethylate solution had to be lifted from the ice bath in order to keep the delivery tip of the machine under the surface of the liquid in the reaction flask. The tube was then shaken by inverting it a few times, and then put back into the bath. Although this process required only one minute for each tube, test with a thermometer showed that the temperature had risen several degrees, and that some better method had to be devised. The possibility of mixing the solution under ice water was suggested, but as this method would have required new apparatus, the following method was tried with very satisfactory results. Ice water from the bath was run continuously through the jacket of the machine by means of a pump run by a small electric motor. Although the exposed circulation was made as short as possible, the temperature of the water returning to the bath had risen several degrees. Even when this current of water was returned to the bath in the vicinity of the thermometer, no change in the temperature could be detected unless the water played directly upon the thermometer. In that part of the bath which contained the reaction flasks, no change in temperature could be detected. The delivery tube of the machine and all exposed connecting tubes were protected by several layers of binding tape, and that liquid in the most exposed part of the delivery tip was discarded just before each 10 c. c. portion was run out. The reaction flask containing the ethylate solution was lifted from the bath in a beaker containing cracked ice and water, and after the alkyl halide solution had been transferred to it, the flask was returned to the bath as rapidly

as possible. Tests made with the thermometer showed that by this method the temperature was kept below 0.5°, and the zero point was quickly reached by shaking the flask two minutes in the bath. For the work with the N/16 and N/32 solutions 40 c. c. portions were used instead of the usual 20 c. c., and the solutions were mixed by inverting and shaking the flasks under the ice water. The corks were protected by rubber fingers over the necks of the flasks. A rise in the temperature of even several tenths of a degree for one minute would have but little effect on the constants, especially those for the dilute solutions for which the time periods were so long.

LITHIUM ETHYLATE AND METHYL IODIDE AT 0°C

Table I—0.5 N Lithium Ethylate and 0.5 N Methyl Iodide at 0°C

$A = 9.98$

t	x	K_V
180	1.782	0.001207
240	2.226	0.001196
300	2.643	0.001200
382	3.156	0.001210
1278	5.946	0.001153
1667	6.580	0.001161

Average = 0.001188

$K_N = 0.002381$

$*K_N = 0.002411$

Table II — 0.5 N Lithium Ethylate and 0.5 N Methyl Iodide at 0°C

$A = 9.98$

t	x	K_V
205	2.016	0.001234
266	2.448	0.001223
347	2.972	0.001222
1353	6.120	0.001172
1430	6.264	0.001180

Average = 0.001206

$K_N = 0.002417$

$*K_N = 0.002425$

* If last two values of K_V are omitted.

Table III—0.5 N. Lithium Ethylate and 1.0 N Methyl Iodide at 0°C

$A = 10.00$ $B = 20.00$

t	x	K_V
180	3.318	0.001232
256	4.240	0.001224
330	4.960	0.001214
424	5.690	0.001195
520	6.304	0.001186

Average = 0.001210

$K_N = 0.002420$

Table IV—0.25 N Lithium Ethylate and 0.5 N Methyl Iodide at 0°C

$A = 10.01$ $B = 20.00$

t	x	K_V
142	1.722	0.0006967
197	2.246	0.0006863
259	2.790	0.0006826
318	3.250	0.0006748
348	3.470	0.0006739

Average = 0.0006828

$K_N = 0.002728$

Table V—0.25 N Lithium Ethylate and 0.5 N Methyl Iodide at 0°C

$A = 10.02$ $B = 20.00$

t	x	K_V
344	3.456	0.0006805
422	3.976	0.0006730
502	4.460	0.0006730
1480	7.612	0.0006420
1608	7.820	0.0006367

Average = 0.0006610

$K_N = 0.002639$

$*K_N = 0.002696$

Table VI—0.25 N Lithium Ethylate and 1.0 N Methyl Iodide at 0°C

$A = 10.02$ $B = 40.00$

t	x	K_V
187	3.840	0.0006831
230	4.444	0.0006803
300	5.256	0.0006714
340	5.656	0.0006770
390	6.104	0.0006630
440	6.500	0.0006597

Average = 0.0006707

$K_N = 0.002678$

* If last two values of K_V are omitted.

Table VII—0.125 N Lithium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.04$ $B = 20.00$

t	x	K_V
1016	4.832	0.0003767
1077	4.992	0.0003746
1140	5.144	0.0003719
1201	5.304	0.0003718
1277	5.488	0.0003710
1347	5.698	0.0003712

Average = 0.0003729

$K_N = 0.002971$

Table VIII—0.125 N Lithium Ethylate and 0.1272 N Methyl Iodide at 0°C

$A = 10.00$ $B = 10.18$

t	x	K_V
1098	2.960	0.0003745
1194	3.136	0.0003742
1289	3.296	0.0003730
1428	3.636	0.0003743
1509	3.656	0.0003732
2619	4.992	0.0003705

Average = 0.0003733

$K_N = 0.002986$

Table IX—0.0625 N Lithium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 9.99$ $B = 40.00$

t	x	K_V
585	3.706	0.0002084
657	4.030	0.0002078
830	4.758	0.0002085
905	4.994	0.0002058
1034	5.422	0.0002050
2108	7.750	0.0002021

Average = 0.0002063

$K_N = 0.003304$

Table X—0.0625 N Lithium Ethylate and 0.1289 N Methyl Iodide at 0°C

$A = 10.01$ $B = 20.63$

t	x	K_V
976	3.198	0.0002144
1066	3.394	0.0002125
1134	3.570	0.0002140
1270	3.858	0.0002130
1378	4.086	0.0002132
2514	6.058	0.0002234
2777	6.154	0.0002088

Average = 0.0002142

$K_N = 0.003423$

Table XI—0.0625 N Lithium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.00$ $B = 40.00$

t	x	K_V
567	3.640	0.0002098
612	3.840	0.0002088
680	4.140	0.0002083
780	4.540	0.0002070
900	5.008	0.0002077
1020	5.416	0.0002072

Average = 0.0002081

$K_N = 0.003330$

Table XII—0.0625 N Lithium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.02$ $B = 40.00$

t	x	K_V
1045	5.444	0.0002036
1135	5.692	0.0002019
1202	5.924	0.0002041
1326	6.244	0.0002031
1496	6.628	0.0002014
2480	8.212	0.0001997

Average = 0.0002023

$K_N = 0.003231$

Table XIII—0.03125 N Lithium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.03$ $B = 80.00$

t	x	K_V
570	4.030	0.0001162
630	4.326	0.0001157
690	4.590	0.0001148
760	4.934	0.0001156
890	5.430	0.0001142
1080	6.070	0.0001129

Average = 0.0001149

$K_N = 0.003665$

Table XIV—0.03125 N Lithium Ethylate and 0.125 N Methyl Iodide at 0°C

$A = 10.00$ $B = 40.00$

t	x	K_V
1067	3.752	0.0001161
1136	3.880	0.0001141
1287	4.312	0.0001166
1463	4.624	0.0001134
2423	6.288	0.0001128
2896	6.880	0.0001126

Average = 0.0001143

$K_N = 0.003657$

Table XV—0.03125 N Lithium Ethylate and 0.25 N Methyl Iodide at 0° C

$A = 10.00$ $B = 80.00$

t	x	K_V
561	3.840	0.0001108
647	4.328	0.0001129
816	5.000	0.0001100

t	x	K_V
898	5.296	0.0001090
983	5.664	0.0001107
1053	5.928	0.0001114
2086	8.168	0.0001087

Average = 0.0001105
K_N = 0.003536

Table XVI—Summary of Lithium Ethylate and Methyl Iodide at 0°C

V	K_N	Average K_N
2	0.002420	
	0.002381	
	(0.002411)	
	0.002417	0.002406
	(0.002425)	(0.002419)
4	0.002728	
	0.002678	
	0.002663	0.002690
	(0.002696)	(0.002700)
8	0.002971	
	0.002986	0.002978
16	0.003304	
	0.003423	
	0.003330	
	0.003231	0.003322
32	0.003665	
	0.003657	
	0.003536	0.003619

Values in parentheses under K_N refer to starred values under tables; average K_N in parentheses, only to the starred values in these tables.

Table XVII—Lithium Ethylate and Methyl Iodide at 0°C

V	a	$1-a$	K_N Found		K_N Calculated		Per. Cent Error	
			a	*b*	*a*	*b*	*a*	*b*
2	0.144	0.856	0.002406	0.002419	0.002440	0.002450	—1.40	—1.30
4	0.220	0.780	0.002690	0.002700	0.002690	0.002697	0.0	+0.10
8	0.312	0.688	0.002978	0.002978	0.002991	0.002994	—0.43	—0.54
16	0.409	0.591	0.003322	0.003322	0.003310	0.003308	+0.36	+0.42
32	0.519	0.481	0.003619	0.003619	0.003668	0.003662	—1.30	—1.20

Values under "b" are calculated on values of K_N in parentheses.

Table XVIII—K_i and K_m for Lithium Ethylate and Methyl Iodide at 0°C

V	K_i		K_m	
	a	*b*	*a*	*b*
2 : 4	0.005590	0.005569	0.001872	0.001891
2 : 8	0.005317	0.005263	0.001918	0.001942
2 : 16	0.005360	0.005531	0.001911	0.001931
2 : 32	0.005174	0.005157	0.001942	0.001960
4 : 8	0.005134	0.005060	0.002001	0.002035
4 : 16	0.005297	0.005264	0.001955	0.001977
4 : 32	0.005115	0.005098	0.002006	0.002024
8 : 16	0.005411	0.005411	0.001875	0.001875
8 : 32	0.005109	0.005109	0.002012	0.002012
16 : 32	0.004922	0.004922	0.002214	0.002214
Average=	0.005243	0.005218	0.001971	0.001986

Values under "b" are calculated from values of Average K_N in parentheses.

SODIUM ETHYLATE AND METHYL IODIDE AT 0°C

Table XIX—1.0 N Sodium Ethylate and 1.0 N Methyl Iodide at 0°C

$A = 9.97$

t	x	K_V
150	3.330	0.003343
180	3.733	0.003325
210	4.088	0.003310
240	4.400	0.003291
1260	8.000	0.003223
1421	8.192	0.003244

Average = 0.003289

$K_N = 0.003299$

Table XX—1.0 N Sodium Ethylate and 1.0 N Methyl Iodide at 0°C

$A = 10.03$

t	x	K_V
120	2.857	0.003319
150	3.319	0.003297
184	3.778	0.003284
197	3.922	0.003259
220	4.218	0.003299
1168	7.904	0.003183

Average = 0.003274

$K_N = 0.003264$

Table XXI—0.5 N Sodium Ethylate and 0.5 N Methyl Iodide at 0°C

$A = 10.00$

t	x	K_V
150	2.058	0.001728
180	2.342	0.001700
210	2.634	0.001703
240	2.896	0.001698
2728	8.200	0.001670

Average = 0.001700

$K_N = 0.003400$

Table XXII—0.5 N Sodium Ethylate and 0.5 N Methyl Iodide at 0°C

$A = 10.02$

t	x	K_V
180	2.372	0.001723
200	2.556	0.001712
230	2.842	0.001721
264	3.122	0.001714
290	3.342	0.001725
1230	6.770	0.001693

Average = 0.001715

$K_N = 0.003420$

Table XXIII—0.5 N Sodium Ethylate and 1.0 N Methyl Iodide at 0°C

$A = 9.98$ $B = 20.00$

t	x	K_V
100	2.782	0.001762
210	4.686	0.001740
260	5.350	0.001750
300	5.764	0.001732
364	6.366	0.001731
430	6.862	0.001721

Average = 0.001739

$K_N = 0.003485$

Table XXIV—0.25 N Sodium Ethylate and 0.50 N Methyl Iodide at 0°C

$A = 10.00$ $B = 20.00$

t	x	K_V
180	2.680	0.0009337
200	2.880	0.0009207
240	3.320	0.0009245
270	3.592	0.0009148
300	3.864	0.0009121
330	4.152	0.0009203
1270	8.120	0.0009056

Average = 0.0009188

$K_N = 0.003679$

Table XXV—0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.00$

t	x	K_V
180	1.400	0.0009044
210	1.608	0.0009126
250	1.840	0.0009020
280	2.020	0.0009042
301	2.132	0.0009003
333	2.328	0.0009112
1280	5.360	0.0009025

Average = 0.0009053

$K_N = 0.003621$

Table XXVI—0.125 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.00$ $B = 20.00$

t	x	K_V
260	2.088	0.0004765
280	2.216	0.0004751
300	2.168	0.0004806
1232	6.160	0.0004779
1326	6.384	0.0004771
1409	6.600	0.0004812

Average = 0.0004781

$K_N = 0.003825$

Table XXVII—0.125 N. Sodium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.00$ $B = 20.00$

t	x	K_V
240	1.968	0.0004813
300	2.384	0.0004816
1275	6.288	0.0004811
1360	6.480	0.0004797
1420	6.608	0.0004785
1640	7.088	0.0004852

Average = 0.0004817

$K_N = 0.003854$

Table XXVIII — 0.0625 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 9.96$ $B = 40.00$

t	x	K_V
988	5.824	0.0002420
1110	6.192	0.0002400
1180	6.480	0.0002457
1265	6.752	0.0002483
1340	6.856	0.0002419
1424	7.112	0.0002458

Average = 0.0002440

$K_N = 0.003919$

Table XXIX—0.0625 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.02$ $B = 40.00$

t	x	K_V
360	2.900	0.0002475
390	3.140	0.0002520
420	3.340	0.0002532
1530	7.396	0.0002479
1620	7.572	0.0002473

Average = 0.0002496

$K_N = 0.003985$

Table XXX—0.0625 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.01$ $B = 40.00$

t	x	K_V
1106	6.418	0.0002565
1180	6.622	0.0002552
1270	6.830	0.0002521
1350	7.070	0.0002548
1447	7.278	0.0002531

Average = 0.0002543

$K_N = 0.004063$

Table XXXI—0.0625 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.00$ $B = 40.00$

t	x	K_V
857	5.520	0.0002544
908	5.720	0.0002548
1031	6.160	0.0002552

Average = 0.0002548

$K_N = 0.004077$

Table XXXII—0.03125 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.01$ $B = 80.00$

t	x	K_V
673	4.970	0.0001321
751	5.338	0.0001319
821	5.562	0.0001287
899	5.874	0.0001284
966	6.314	0.0001353
1095	6.714	0.0001337

Average = 0.0001317

$K_N = 0.004212$

Table XXXIII — 0.03125 N Sodium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.02$ $B = 80.00$

t	x	K_V
220	2.032	*0.0001305
270	2.428	0.0001308
300	2.660	0.0001310
1327	7.180	0.0001258
1493	7.644	0.0001283

Average = 0.0001293

$K_N = 0.004130$

* $A = 10.12$

Table XXXIV — 0.03125 N Sodium Ethylate and 0.125 N Methyl Iodide at 0°C

$A = 10.02$ $B = 40.00$

t	x	K_V
1462	5.124	0.0001324
1670	5.524	0.0001306
1832	5.804	0.0001296
3020	7.476	0.0001288

Average = 0.0001304

$K_N = 0.004165$

Table XXXV—Summary of Sodium Ethylate and Methyl Iodide at 0°C

V	K_N	Average K_N
1	0.003299	
	0.003264	0.003281
2	0.003400	
	0.003420	
	0.003485	0.003435
4	0.003679	
	0.003621	0.003650
8	0.003825	
	0.003854	0.003840
16	0.003919	
	0.003985	
	0.004063	
	0.004077	0.004011
32	0.004212	
	0.004130	0.004169
	0.004165	

Table XXXVI—Sodium Ethylate and Methyl Iodide at 0° C

V	a	$1 - a$	K_N Found	K_N Calculated	Per Cent Error
1	0.136	0.864	0.003281	0.003282	—0.03
2	0.237	0.763	0.003435	0.003466	—0.90
4	0.335	0.665	0.003650	0.003645	+0.13
8	0.435	0.565	0.003840	0.003828	+0.31
16	0.531	0.469	0.004011	0.004004	+0.17
32	0.633	0.367	0.004169	0.004190	—0.50

Table XXXVII—K_i and K_m for Sodium Ethylate and Methyl Iodide at 0° C

V	K_i	K_m
1 : 2	0.004598	0.003074
1 : 4	0.004883	0.003010
1 : 8	0.004896	0.003027
1 : 16	0.004878	0.003030
1 : 32	0.004824	0.003038
2 : 4	0.005109	0.002915
2 : 8	0.004995	0.002950
2 : 16	0.004930	0.002970
2 : 32	0.004849	0.002995
4 : 8	0.004914	0.003014
4 : 16	0.004874	0.003033
4 : 32	0.004808	0.003066
8 : 16	0.004846	0.003065
8 : 32	0.004778	0.003116
16 : 32	0.004737	0.003188
	Average = 0.004861	0.003033

POTASSIUM ETHYLATE AND METHYL IODIDE AT 0°

Table XXXVIII—0.25 N Potassium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.00$

t	x	K_V
110	0.972	0.000980
190	1.600	0.001002
290	2.268	0.001015
350	2.604	0.001006
390	2.804	0.000997
1430	5.936	0.001021
1590	6.196	0.001024

Average = 0.001006

$K_N = 0.004024$

Table XXXIX—0.25 N. Potassium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.02$

t	x	K_V
120	1.086	0.001014
180	1.506	0.000984
300	2.294	0.000991
440	3.026	0.000985
520	3.418	0.000997
373	2.710	0.000995
1271	5.626	0.001010

Average = 0.000997

$K_N = 0.003982$

Table XL—0.25 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 9.97$ $B = 20.00$

t	x	K_V
120	2.066	0.001020
150	2.490	0.001022
180	2.870	0.001019
190	2.978	0.001012
210	3.234	0.001021

Average = 0.001019

$K_N = 0.004088$

Table XLI—0.1875 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 9.98$ $B = 26.67$

t	x	K_V
90	1.639	0.0007705
130	2.279	0.0007813
160	2.679	0.0007724
180	2.940	0.0007712
220	3.436	0.0007721
260	3.890	0.0007732

Average = 0.0007735

$K_N = 0.004133$

$K_N = 0.004123$

Table XLII—0.1875 N Potassium Ethylate and 0.25 N Methyl Iodide at 0°C

$A = 10.02$ $B = 13.33$

t	x	K_V
120	1.119	0.0007755
150	1.375	0.0007818
200	1.753	0.0007769
250	2.116	0.0007790
320	2.564	0.0007755
370	2.857	0.0007728
480	3.417	0.0007630

Average = 0.0007749

$K_N = 0.004124$

Table XLIII—0.125 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 10.02$ $B = 40.00$

t	x	K_V
260	4.004	0.0005278
320	4.692	0.0005292
380	5.260	0.0005304
450	5.820	0.0005293
503	6.204	0.0005288

Average = 0.0005291

$K_N = 0.004224$

Table XLIV—0.125 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 10.00$ $B = 40.00$

t	x	K_V
190	3.192	0.0005285
240	3.832	0.0005311
290	4.376	0.0005282
330	4.792	0.0005299
360	5.064	0.0005280
390	5.360	0.0005331
460	5.880	0.0005271

Average = 0.0005294

$K_N = 0.004235$

Table XLV—0.125 N. Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 10.00$ $B = 40.00$

t	x	K_V
160	2.784	0.0005291
190	3.200	0.0005301
230	3.720	0.0005326
250	3.968	0.0005345
267	4.152	0.0005328
300	4.512	0.0005336

Average = 0.0005321

$K_N = 0.004257$

Table XLVI—0.09375 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 10.00$ $B = 53.33$

t	x	K_V
120	2.267	0.0004108
180	3.142	0.0004056
220	3.685	0.0004070
260	4.187	0.0004089
365	5.264	0.0004068
420	5.733	0.0004055

Average = 0.0004074

$K_N = 0.004347$

Table XLVII — 0.09375 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 10.04$ $B = 53.33$

t	x	K_V
180	3.192	0.0004135
210	3.598	0.0004130
360	4.206	0.0004109
320	4.824	0.0004058

Average = 0.0004108

$A = 100.00$ $B = 53.33$

Table XLVIII — 0.09375 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 10.00$ $B = 53.33$

t	x	K_V
120	2.256	0.0004089
180	3.131	0.0004039
220	3.664	0.0004039
270	4.293	0.0004076
420	5.723	0.0004042

Average = 0.0004057

$K_N = 0.004329$

Table XLIX—0.0625 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 10.00$ $B = 80.00$

t	x	K_V
120	2.376	0.0002836
150	2.856	0.0002827
190	3.448	0.0002821
250	4.200	0.0002803
300	4.728	0.0002757
360	5.376	0.0002784
420	5.904	0.0002774

Average = 0.0002800

$K_N = 0.004480$

Table L—0.0625 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 10.08$ $B = 80.00$

t	x	K_V
180	3.272	0.0002808
230	3.928	0.0002778
290	4.672	0.0002796
350	5.304	0.0002794
430	6.008	0.0002777
500	6.544	0.0002774

Average = 0.0002788

$K_N = 0.004424$

Table LI—0.0625 N Potassium Ethylate and 0.1342 N Methyl Iodide at 0°

$A = 10.07$ $B = 21.47$

t	x	K_V
835	3.638	0.0002777
910	3.838	0.0002745
935	3.894	0.0002726
1010	4.134	0.0002746
1080	4.302	0.0002726
1240	4.702	0.0002718
1365	4.966	0.0002694

Average = 0.0002733

$K_N = 0.004343$

Table LII—0.0625 N Potassium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.03$ $B = 40.00$

t	x	K_V
600	4.526	0.0002677
630	4.734	0.0002722
670	4.902	0.0002697
720	5.174	0.0002727
780	5.406	0.0002699

Average = 0.0002704

$K_N = 0.004300$

Table LIII—0.0625 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 10.03$ $B = 80.00$

t	x	K_V
130	2.478	0.0002781
180	3.152	0.0002715
210	3.598	0.0002718
260	4.302	0.0002783
340	5.214	0.0002808
420	5.902	0.0002768

Average = 0.0002762

$K_N = 0.004405$

Table LIV—0.03125 N Potassium Ethylate and 0.125 N Methyl Iodide at 0°

$A = 10.02$ $B = 40.00$

t	x	K_V
890	3.764	0.0001397
1000	4.092	0.0001393
1110	4.444	0.0001409
1200	4.604	0.0001372
1320	4.980	0.0001402
1412	5.252	0.0001417

Average = 0.0001398

$K_N = 0.004466$

Table LV—0.03125 N Potassium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.00$ $B = 80.00$

t	x	K_V
650	4.936	0.0001355
700	5.264	0.0001385
730	5.456	0.0001405
760	5.584	0.0001400
800	5.712	0.0001379
840	5.888	0.0001381
990	6.424	0.0001363

Average = 0.0001381

$K_N = 0.004419$

Table LVI—0.03125 N Potassium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.03$ $B = 80.00$

t	x	K_V
180	1.830	0.0001420
240	2.350	0.0001416
320	2.894	0.0001360
360	3.230	0.0001383
420	3.742	0.0001430
480	4.094	0.0001409

Average = 0.0001403

$K_N = 0.004476$

Table LVII—0.03125 N Potassium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.01$ $B = 80.00$

t	x	K_V
160	1.642	0.0001415
220	2.258	0.0001475
270	2.554	0.0001390
340	3.130	0.0001409
390	3.554	0.0001441
450	3.922	0.0001420

Average = 0.0001425

$K_N = 0.004556$

Table LVIII—0.03125 N Potassium Ethylate and 0.25 N Methyl Iodide at 0°

$A = 10.00$ $B = 80.00$

t	x	K_V
140	1.448	0.0001409
200	1.952	0.0001374
250	2.424	0.0001410
320	2.960	0.0001398
380	3.440	0.0001419
430	3.736	0.0001394

Average $= 0.0001401$

$K_N = 0.004482$

Table LIX—0.03125 N Potassium Ethylate and 0.50 N Methyl Iodide at 0°

$A = 10.00$ $B = 160.00$

t	x	K_V
190	3.528	0.0001446
220	3.968	0.0001454
270	4.568	0.0001433
360	5.480	0.0001404
420	6.080	0.0001423

Average $= 0.0001432$

$K_N = 0.004582$

Table LX—Summary of Potassium Ethylate and Methyl Iodide at 0°

V	K_N	Average K_N
4	0.004024	
	0.003982	
	0.004088	0.004031
16/3	0.004123	
	0.004124	0.004124
8	0.004224	
	0.004235	
	0.004258	0.004239
32/3	0.004347	
	0.004362	
	0.004329	0.004346
16	0.004480	
	0.004300	
	0.004424	
	0.004343	
	0.004405	0.004390

V	K_N	Average K_N
32	0.004466	
	0.004419	
	0.004582	
	0.004476	
	0.004556	0.004500

Table LXI—Potassium Ethylate and Methyl Iodide at 0°C

V	a	$1-a$	K_N Found	K_N Calculated	Per Cent. Error
4	0.365	0.635	0.004031	0.004055	—0.62
16/3	0.401	0.599	0.004124	0.004123	+0.02
8	0.459	0.541	0.004239	0.004233	+0.12
32/3	0.491	0.509	0.004346	0.004292	+0.26
16	0.546	0.454	0.004390	0.004397	—0.10
32	0.637	0.363	0.004497	0.004568	—1.55

Table LXII—K_i and K_m for Potassium Ethylate and Methyl Iodide at 0°

V	K_i	K_m
4 : 8	0.00543	0.00320
4 : 32/3	0.00562	0.00310
4 : 16	0.00528	0.00329
4 : 32	0.00513	0.00340
16/3 : 32/3	0.00564	0.00306
16/3 : 16	0.00522	0.00335
16/3 : 32	0.00508	0.00348
8 : 16	0.00517	0.00345
8 : 32	0.00502	0.00359
16 : 32	0.00493	0.00377
	Average = 0.00525	0.00337

SODIUM ETHYLATE AND METHYL IODIDE AT 25°

Table LXIII—0.5 N Sodium Ethylate and 0.5 N Methyl Iodide at 25°C

$A = 10.00$

t	x	K_V
20	4.343	0.03839
30	5.337	0.03815
40	5.999	0.03745
50	6.495	0.03714
60	6.901	0.03711
70	7.187	0.03650

Average = 0.03746

$K_N = 0.07492$

Table LXIV—0.5 N Sodium Ethylate and 0.5095 N Methyl Iodide at 25°C

$A = 10.00$ $B = 10.19$

t	x	K_V
15	3.657	0.03715
24	4.830	0.03786
33	5.600	0.03745
42	6.166	0.03691
51	6.586	0.03634
69	7.207	0.03564
97	7.815	0.03500

Average = 0.03662

$K_N = 0.07324$

Table LXV—0.5 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 20.00$ $B = 10.00$

t	x	K_V
15	4.044	0.03894
25	5.492	0.03805
35	6.476	0.03723
55	7.818	0.03722
65	8.196	0.03646
75	8.520	0.03613

Average = 0.03735

$K_N = 0.07471$

Table LXVI—0.5 N Sodium Ethylate and 0.5 N Methyl Iodide at 25°C

$A = 9.989$

t	x	K_V
10	2.891	0.04073
20	4.375	0.03896
30	5.367	0.03870
40	6.027	0.03803
50	6.527	0.03770
60	6.889	0.03703
70	7.175	0.03642

Average = 0.03822

$K_N = 0.07652$

Table LXVII—0.5 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 20.04$ $B = 10.00$

t	x	K_V
20	4.780	0.03768
30	6.032	0.03766
37	6.676	0.03755
43	7.120	0.03740
50	7.520	0.03687
59	7.932	0.03626
68	8.308	0.03643

Average = 0.03712

$K_N = 0.07409$

Table LXVIII—0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 10.00$

t	x	K_V
10	1.685	0.02026
20	2.909	0.02051
30	3.760	0.02008
40	4.446	0.02001
50	5.000	0.02000
60	5.430	0.01980
70	5.793	0.01967

Average = 0.02005

$K_N = 0.08020$

Table LXIX—0.25 N Sodium Ethylate and 0.50 N Methyl Iodide at 25°C

$A = 10.02$ $B = 20.00$

t	x	K_V
15	4.152	0.02024
25	5.668	0.02009
35	6.682	0.01988
45	7.418	0.01972
55	7.956	0.01934
65	8.363	0.01942
75	8.698	0.01947

Average = 0.01974

$K_N = 0.07880$

Table LXX—0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 9.956$

t	x	K_V
20	2.868	0.02023
25	3.340	0.02019
30	3.758	0.02021
40	4.453	0.02023
50	4.980	0.02002
60	5.420	0.01991

Average = 0.02013

$K_N = 0.08086$

Table LXXI—0.25 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 10.01$

t	x	K_V
20	2.918	0.02057
25	3.354	0.02015
30	3.768	0.02012
40	4.455	0.02005
46	4.795	0.01998
52	5.076	0.01978

Average = 0.02011

$K_N = 0.08035$

Table LXXII—0.125 N Sodium Ethylate and 0.125 N Methyl Iodide at 25°C

$A = 10.00$

t	x	K_V
40	2.959	0.01051
55	3.691	0.01064
70	4.223	0.01045
80	4.575	0.01054
90	4.852	0.01047
100	5.111	0.01045

Average = 0.01051

$K_N = 0.08406$

Table LXXIII—0.125 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 10.00$ $B = 20.00$

t	x	K_V
15	2.594	0.01075
25	3.836	0.01082
35	4.830	0.01094
45	5.548	0.01075
55	6.163	0.01072
65	6.686	0.01072
75	7.103	0.01067

Average = 0.01077

$K_N = 0.08616$

Table LXXIV—0.125 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 10.03$ $B = 20.00$

t	x	K_V
20	3.318	0.01107
26	3.982	0.01098
34	4.734	0.01090
42	5.382	0.01091
47	5.734	0.01091
57	6.318	0.01084

Average = 0.01094

$K_N = 0.08722$

Table LXXV—0.125 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 10.00$ $B = 20.00$

t	x	K_V
15	2.648	0.01103
25	3.848	0.01088
32	4.560	0.01094
38	5.080	0.01095
46	5.656	0.01090
52	5.992	0.01073
58	6.312	0.01066

Average = 0.01087

$K_N = 0.08696$

Table LXXVI—0.0625 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 10.00$ $B = 41.00$

t	x	K_V
15	2.889	0.005475
25	4.311	0.005842
35	5.366	0.005722
45	6.180	0.005725
55	6.884	0.005759
65	7.435	0.005934

Average = 0.005754

$K_N = 0.09206$

Table LXXVII — 0.0625 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 10.00$ $B = 40.00$

t	x	K_V
15	2.800	0.005678
25	4.181	0.005746
35	5.256	0.005771
45	6.105	0.005768
55	7.000	0.006122
65	7.436	0.005911
75	7.724	0.005622

Average = 0.005802

$K_N = 0.09198$

Table LXXVIII—0.03125 N Sodium Ethylate and 0.25 N Methyl Iodide at 25°C

$A = 9.912$ $B = 80.00$

t	x	K_V
15	3.001	0.003029
25	4.550	0.003144
35	5.607	0.003075
45	6.305	0.003088
55	7.184	0.003074
65	7.741	0.003081

Average = 0.003082

$K_N = 0.09948$

Table LXXIX — 0.03125 N Sodium Ethylate and 0.125 N Methyl Iodide at 25°C

$A = 10.07$ $B = 40.00$

t	x	K_V
55	4.876	0.003252
80	5.893	0.003029
100	6.783	0.003143
135	7.732	0.003104
150	8.038	0.003085
180	8.482	0.003007
		Average = 0.003103
		$K_N = 0.09860$

Table LXXX—0.03125 N Sodium Sthylate and 0.25 N Methyl Iodide at 25°C

$A = 10.00$ $B = 80.00$

t	x	K_V
20	3.780	0.003045
25	4.467	0.003053
30	5.168	0.003144
35	5.504	0.002972
40	6.120	0.003098
45	6.595	0.003145
50	6.956	0.003137
		Average = 0.003085
		$K_N = 0.09872$

Table LXXXI—Summary of Sodium Ethylate and Methyl Iodide at 25°C

V	K_N	Average K_N
2	0.07492	
	0.07324	
	0.07471	
	0.07652	
	0.07409	0.07470
4	0.08020	
	0.07880	
	0.08086	
	0.08035	0.08005
8	0.08406	
	0.08616	
	0.08722	
	0.08696	0.08610
16	0.09206	
	0.09198	0.09202
32	0.09872	
	0.09948	
	0.09860	0.09893

Table LXXXII—Sodium Ethylate and Methyl Iodide at 25° C

V	a	$1 - a$	K_N Found	K_N Calculated	Per Cent Error
2	0.234	0.766	0.07470	0.07466	+0.053
4	0.312	0.688	0.08005	0.08026	—0.26
8	0.393	0.607	0.08610	0.08590	+0.23
16	0.481	0.519	0.09202	0.09191	+0.12
32	0.584	0.416	0.09893	0.09909	—0.16

Table LXXXIII—K_i and K_m for Sodium Ethylate and Methyl Iodide at 25° C

V	K_i	K_m
2 : 4	0.1272	0.05865
2 : 8	0.1296	0.05792
2 : 16	0.1284	0.05829
2 : 32	0.1277	0.05850
4 : 8	0.1313	0.05674
4 : 16	0.1288	0.05795
4 : 32	0.1278	0.05839
8 : 16	0.1269	0.05966
8 : 32	0.1269	0.05970
16 : 32	0.1268	0.05994
Average =	0.1281	0.05857

SALT EFFECT

SODIUM ETHYLATE, METHYL IODIDE AND SODIUM IODIDE AT 25°C

Table LXXXIV—0.25 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.25 N Sodium Iodide at 25°C

$A = 9.971$

t	x	K_V
15	2.067	0.01743
25	3.031	0.01747
31	3.500	0.01744
40	4.097	0.01744
48	4.528	0.01733
57	4.953	0.01732
66	5.307	0.01724

Average = 0.01738

$K_N = 0.06972$

Table LXXXV—0.25 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.25 N Sodium Iodide at 25°C

$A = 10.01$

t	x	K_V
15	2.078	0.01747
23	2.874	0.01751
31	3.506	0.01739
41	4.170	0.01742
48	4.547	0.01734
56	4.930	0.01734
64	5.262	0.01732

Average = 0.01740

$K_N = 0.06952$

Table LXXXVI—0.25 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.75 N Sodium Iodide

$A = 9.98$

t	x	K_V
15	1.828	0.01495
23	2.538	0.01483
31	3.144	0.01484
41	3.750	0.01468
50	4.233	0.01473
60	4.657	0.01458
71	5.098	0.01471

Average = 0.01476

$K_N = 0.05915$

Table LXXXVII — 0.25 N Sodium Ethylate and 0.25 N Methyl Iodide and 0.75 N Sodium Iodide

$A = 9.98$

t	x	K_V
15	1.864	0.01531
24	2.628	0.01489
34	3.344	0.01482
43	3.864	0.01469
53	4.372	0.01471
63	4.804	0.01473
72	5.120	0.01463

Average = 0.01483

$K_N = 0.05942$

Table LXXXVIII—0.125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.125 N Sodium Iodide

$A = 9.98$ $B = 20.00$

t	x	K_V
15	2.294	0.009251
20	3.036	0.009862
28	3.778	0.009473
34	4.337	0.009540
42	4.920	0.009409
50	5.484	0.009498
58	5.916	0.009404

Average = 0.009491

$K_N = 0.07608$

Table LXXXIX — 0.125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.125 N Sodium Iodide

$A = 9.976$ $B = 20.00$

t	x	K_V
15	2.326	0.009408
22	3.188	0.009560
29	3.906	0.009591
37	4.605	0.009613
44	5.121	0.009596
52	5.624	0.009555
59	5.988	0.009461

Average = 0.009541

$K_N = 0.07651$

Table XC—0.125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.375 N Sodium Iodide

$A = 9.99$ $B = 20.00$

t	x	K_V
15	2.095	0.008295
23	2.951	0.008263
32	3.785	0.008307
39	4.356	0.008369
47	4.905	0.008362
54	5.311	0.008312
60	5.655	0.008356

Average = 0.008323

$K_N = 0.06664$

Table XCI—0.125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.375 N Sodium Iodide

$A = 10.01$ $B = 20.00$

t	x	K_V
15	2.102	0.008325
23	2.978	0.008358
30	3.656	0.008433
38	4.287	0.008380
47	4.899	0.008340
55	5.390	0.008362
63	5.818	0.008374

Average = 0.008367

$K_N = 0.6689$

Table XCII — 0.125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.875 N Sodium Iodide

$A = 9.959$ $B = 20.00$

t	x	K_V
15	1.879	0.007299
23	2.634	0.007154
33	3.499	0.007227
40	3.993	0.007181
49	4.556	0.007142
57	4.999	0.007122
64	5.351	0.007116

Average = 0.007177

$K_N = 0.05765$

Table XCIII—0.125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.875 N Sodium Iodide

$A = 10.01$ $B = 20.00$

t	x	K_V
15	1.818	0.007023
25	2.774	0.007022
35	3.590	0.007051
44	4.250	0.007144
54	4.818	0.007066
63	5.290	0.007070
72	5.686	0.007025

Average = 0.007057

$K_N = 0.05640$

Table XCIV—0.0625 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.0625 N Sodium Iodide

$A = 10.10$ $B = 40.00$

t	x	K_V
15	2.626	0.005250
22	3.550	0.005220
28	4.242	0.005218
34	4.886	0.005273
40	5.425	0.005265
46	5.852	0.005197
52	6.276	0.005199

Average = 0.005232

$K_N = 0.08287$

Table XCV—0.0625 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.0625 N Sodium Iodide

$A = 10.03$ $B = 40.00$

t	x	K_V
15	2.604	0.005203
21	3.450	0.005279
27	4.156	0.005271
33	4.736	0.005201
38	5.214	0.005230
44	5.694	0.005209
51	6.150	0.005135

Average = 0.005218

$K_N = 0.08323$

Table XCVI—0.0625 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.0625 N Sodium Iodide

$A = 10.03$ $B = 40.00$

t	x	K_V
10	1.893	0.005357
20	3.305	0.005226
30	4.426	0.005162
40	5.372	0.005188
50	6.106	0.005150
60	6.731	0.005153
70	7.219	0.005107

Average = 0.005192

$K_N = 0.08281$

Table XCVII—0.0625 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.1875 N Sodium Iodide

$A = 10.08$ $B = 40.00$

t	x	K_V
15	2.336	0.004568
22	3.200	0.004570
28	3.856	0.004580
34	4.468	0.004628
41	5.040	0.004587
49	6.640	0.004590
58	6.184	0.004545

Average = 0.004581

$K_N = 0.07270$

Table XCVIII—0.0625 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.1875 N Sodium Iodide

$A = 10.00$ $B = 40.00$

t	x	K_V
15	2.280	0.004444
22	3.184	0.004548
28	3.832	0.004552
34	4.428	0.004581
41	5.024	0.004581
49	5.600	0.004557
57	6.144	0.004595

Average = 0.004551

$K_N = 0.07282$

Table XCIX—0.0625 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.4375 N Sodium Iodide

$A = 10.04$ $B = 40.00$

t	x	K_V
15	2.160	0.004171
21	2.848	0.004144
28	3.576	0.004148
35	4.200	0.004125
42	4.784	0.004146
49	5.248	0.004095
56	5.680	0.004074

Average = 0.004129

$K_N = 0.06582$

Table C—0.0625 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.4375 N Sodium Iodide

$A = 10.04$ $B = 40.00$

t	x	K_V
15	2.152	0.004152
22	2.944	0.004120
29	3.659	0.004128
36	4.284	0.004123
43	4.882	0.004175
50	5.360	0.004150
56	5.720	0.004122

Average = 0.004138

$K_N = 0.06596$

Table CI—0.0625 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.9375 N Sodium Iodide

$A = 10.00$ $B = 40.00$

t	x	K_V
15	1.720	0.003322
25	2.766	0.003361
34	3.592	0.003439
44	4.357	0.003460
53	4.897	0.003409
62	5.380	0.003374

Average = 0.003394

$K_N = 0.05430$

Table CII—0.0625 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.9375 N Sodium Iodide

$A = 9.99$ $B = 40.00$

t	x	K_V
15	1.826	0.003442
24	2.738	0.003458
33	3.550	0.003490
41	4.186	0.003511
50	4.786	0.003492
59	5.290	0.003459
68	5.770	0.003455

Average = 0.003472

$K_N = 0.05561$

Table CIII—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.03125 N Sodium Iodide

$A = 10.00$ $B = 80.00$

t	x	K_V
15	2.840	0.002836
25	4.213	0.002817
35	5.320	0.002819
45	6.226	0.002836
55	6.932	0.002834
65	7.456	0.002794
75	7.859	0.002739

Average = 0.002811

$K_N = 0.08995$

Table CIV—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.03125 N Sodium Iodide

$A = 10.00$ $B = 80.00$

t	x	K_V
15	2.880	0.002886
25	4.236	0.002836
35	5.360	0.002852
45	6.162	0.002786
55	6.904	0.002811
65	7.432	0.002774
75	7.859	0.002740

Average = 0.002813

$K_N = 0.09002$

Table CV—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.09375 N Sodium Iodide

$A = 10.00$ $B = 80.00$

t	x	K_V
20	3.160	0.002425
30	4.340	0.002445
40	5.289	0.002444
50	6.041	0.002423
60	6.709	0.002436
70	7.246	0.002439

Average = 0.002436

$K_N = 0.07795$

Table CVI—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.09375 N Sodium Iodide

$A = 10.00$ $B = 80.00$

t	x	K_V
10	1.763	0.002453
20	3.205	0.002468
30	4.459	0.002438
40	5.454	0.002554
50	6.155	0.002502
60	6.814	0.002510
70	7.330	0.002499

Average = 0.002489

$K_N = 0.07964$

Table CVII—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.09375 N Sodium Iodide

$A = 10.07$ $B = 80.00$

t	x	K_V
15	2.518	0.002455
22	3.470	0.002474
28	4.134	0.002444
35	4.870	0.002460
41	5.374	0.002434
49	5.974	0.002415

Average = 0.002447

$K_N = 0.07776$

Table CVIII—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.21875 N Sodium Iodide

$A = 10.00$ $B = 80.00$

t	x	K_V
15	2.224	0.002126
20	2.880	0.002163
26	3.592	0.002192
32	4.224	0.002207
40	4.856	0.002150
49	5.648	0.002211

Average = 0.002176

$K_N = 0.06964$

Table CIX—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.21875 N Sodium Iodide

$A = 10.05$ $B = 80.00$

t	x	K_V
20	2.898	0.002178
25	3.450	0.002162
30	3.962	0.002156
35	4.442	0.002159
40	4.842	0.002136
45	5.162	0.002087
50	5.594	0.002128

Average = 0.002144

$K_N = 0.06832$

Table CX—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.46875 N Sodium Iodide

$A = 9.944$ $B = 80.00$

t	x	K_V
14	1.816	0.001811
22	2.664	0.001793
32	3.840	0.001946
40	4.544	0.001958
49	5.240	0.001971
58	5.848	0.001984

Average = 0.001911

$K_N = 0.06148$

Table CXI—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.46875 N Sodium Iodide

$A = 10.01$ $B = 80.00$

t	x	K_V
15	2.010	0.001894
24	3.090	0.001965
40	4.482	0.001916
48	5.170	0.001965
56	5.594	0.001904
63	6.074	0.001939

Average = 0.001939

$K_N = 0.06199$

Table CXII—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.96875 N Sodium Iodide

$A = 9.99$ $B = 80.00$

t	x	K_V
21	2.454	0.001704
29	3.150	0.001666
37	3.886	0.001707
46	4.486	0.001670
54	5.096	0.001710
64	5.574	0.001659

Average = 0.001686

$K_N = 0.05400$

Table CXIII—0.03125 N Sodium Ethylate, 0.25 N Methyl Iodide and 0.96875 N Sodium Iodide

$A = 10.02$ $B = 80.00$

t	x	K_V
13	1.492	0.001568
21	2.324	0.001587
30	3.220	0.001654
38	3.788	0.001606
46	4.348	0.001597
55	5.044	0.001652
63	5.556	0.001674

Average = 0.001620

$K_N = 0.05173$

Table CXIV—Summary of Sodium Ethylate, Methyl Iodide and Sodium Iodide at 25°C

V		K_N	Average K_N
Sodium Ethylate	Sodium Iodide		
32	32	0.08995	
		0.09002	0.08998
32	32/3	0.07795	
		0.07964	
		0.07776	0.07845
32	32/7	0.06964	
		0.06832	0.06898
32	32/15	0.06148	
		0.06199	0.06173
32	32/31	0.05400	
		0.05173	0.05287
16	16	0.08323	
		0.08287	
		0.08281	0.08297
16	16/3	0.07270	
		0.07282	0.07276
16	16/7	0.06596	
		0.06582	0.06589
16	16/15	0.05430	
		0.05561	0.05496
8	8	0.07608	
		0.07651	0.07630
8	8/3	0.06664	
		0.06689	0.06676
8	8/7	0.05765	
		0.05640	0.05702
4	4	0.06972	
		0.06952	0.06962
4	4/3	0.05915	
		0.05942	0.05928

Table CXV—Sodium Ethylate, Methyl Iodide and Sodium Iodide at 25°C

Sodium Ethylate	Sodium Iodide	Sodium Ethylate in Mixture	a	$1-a$	K_N Found	K_N Calculated	Per Cent Difference
32	32	16	0.481	0.519	0.08998	0.09191	—2.10
32	32/3	8	0.393	0.607	0.07845	0.08590	—8.67
32	32/7	4	0.312	0.688	0.06898	0.08026	—14.05
32	32/15	2	0.234	0.766	0.06173	0.07466	—17.32
32	32/31	1	0.148	0.852	0.05287	0.06886	—23.54
16	16	8	0.393	0.607	0.08297	0.08590	—3.41
16	16/3	4	0.312	0.688	0.07276	0.08026	—9.34
16	16/7	2	0.234	0.766	0.06589	0.07466	—11.74
16	16/15	1	0.148	0.852	0.05496	0.06886	—20.19
8	8	4	0.312	0.688	0.07630	0.08026	—4.93
8	8/3	2	0.234	0.766	0.06676	0.07466	—10.58
8	8/7	1	0.148	0.852	0.05702	0.06886	—17.19
4	4	2	0.234	0.766	0.06962	0.07466	—6.75
4	4/3	1	0.148	0.852	0.05928	0.06886	—13.91

Table CXVI—Sodium Ethylate, Methyl Iodide and Sodium Iodide at 25

Sodium Ethylate	Sodium Iodide	V Sodium Ethylate in Mixture	α and α'	$1 - \alpha$	K_N Found	K_N Calculated	Per Cent Error
32	32	16	0.481	0.519	0.08998	0.0902	—0.2
32	32/3	8	0.393	0.607	0.07845	0.0828	—5.2
32	32/7	4	0.312	0.688	0.06898	0.0748	—7.7
32	32/15	2	0.234	0.766	0.06173	0.0658	—6.2
32	32/31	1	0.148	0.852	0.05287	0.0548	—3.4
16	16	8	0.393	0.607	0.08297	0.0833	—0.4
16	16/3	4	0.312	0.688	0.07276	0.0752	—3.2
16	16/7	2	0.234	0.766	0.06589	0.0661	—0.3
16	16/15	1	0.148	0.852	0.05496	0.0551	—0.5
8	8	4	0.312	0.688	0.07630	0.0761	+0.3
8	8/3	2	0.234	0.766	0.06676	0.0669	—0.2
8	8/7	1	0.148	0.852	0.05702	0.0557	+2.3
4	4	2	0.234	0.766	0.06962	0.0683	+2.0
4	4/3	1	0.148	0.852	0.05928	0.0570	+4.0

CONCLUSIONS

1. It has been shown that methyl iodide reacts at 0° with sodium, potassium and lithium ethylates. The velocity can be expressed as functions of the concentrations of both the ethylate ions and the nonionized salts.

2. If the ethylate ion reacts independently with the methyl iodide, we should obtain from all three ethylates the same value for K_i, the reaction velocity of unit concentrations of the ethylate ions and methyl iodide. But different values might be found for the reaction velocities of the three nonionized ethylates, which, of course, do not have the same physical and chemical properties. In confirmation of this theory, we find the values 0.00525, 0.00486 and 0.00522 for K_i, and the values 0.00337, 0.00303 and 0.00199 for K_m.

3. The "salt effect" produced by sodium iodide on the reactions of sodium ethylate and methyl iodide at 25°, has been studied in various concentrations. It has been shown that, besides the "normal salt effect" due to the change in the ionization of the sodium ethylate, produced by the added sodium iodide, there is in addition, a slight "negative abnormal salt effect" which can be expressed as a function of the concentrations of the ethylate ions and the iodide ions.

BIOGRAPHY

Bessie Marion Brown, the author of this dissertation, was born in Rye, New Hampshire, July 31, 1884. She received her early education in the public schools of that town, and her high school training at Newburyport, Massachusetts, and the degree of B. S. from Simmons College, Boston, Massachusetts, in 1907. After holding an instructorship in chemistry at the latter institution for four years, she entered Johns Hopkins University in 1911 as a graduate student in chemistry with physical chemistry and elementary applied electricity as minor subjects. In 1911–12 she was appointed a university scholar.